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Short communication

Preparation and electrical properties of $(1-x)Ba(Fe_{0.5}Nb_{0.5})O_3$–$xBaTiO_3$ ceramics

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Abstract

$(1-x)Ba(Fe_{0.5}Nb_{0.5})O_3$–$xBaTiO_3$ ceramics with giant dielectric constants and low losses were prepared by the conventional solid-state method. The phase structure, microstructures, electrical properties of the ceramics were investigated. The results show that the ceramics are of monoclinic structure and possess dense and fine microstructures. The incorporation of $BaTiO_3$ can significantly reduce the dielectric loss and improve the frequency and temperature stability of the electrical properties of $Ba(Fe_{0.5}Nb_{0.5})O_3$.

Keywords: D. Perovskites; Dielectrics; Ceramics

1. Introduction

With the rapid development of microelectronics industry, the materials, which can meet the requirements of miniaturization and integration of chip electronic components, are needed. As driven by the impetus of smaller and smaller feature sizes of devices in microelectronics, materials with giant dielectric constants are always attracting the attention of researchers. From the materials science point of view, the fundamental researches on materials with giant dielectric constants are very interesting and necessary as well. Some common dielectric materials with high dielectric constants, such as lead zirconate titanate (PZT), contain lead that inevitably causes environmental problems due to the toxicity of lead oxide. Therefore, it is necessary and urgent to search for lead-free materials with excellent dielectric properties, which should be comparable to those found in the lead-based ceramics. In such a case, much attention has been attracted by some lead-free materials with giant dielectric constants, such as cubic perovskite-related compound $CaCu_3Ti_4O_{12}$ [1–3], some Fe-containing complex perovskites $A(Fe_{1/2}B_{1/2})O_3$ (A = Ba, Sr, Ca; B = Nb, Ta, Sb) [4,5], Li, Ti co-doped NiO [6–8], ferroelectric superlattices [9] and ferroelectric/metal composites [10,11].

Complex perovskite $Ba(Fe_{0.5}Nb_{0.5})O_3$ (BFN) with giant dielectric constant has been paid much attention [12]. BFN was first synthesized via solid-state reaction by Tezuka et al. in 2000 [13]. After that, many researchers have studied the properties of BFN, including, Saha and Sinha [14], Charoenthai et al. [15], Ke et al. [16], Eitssayeam et al. [17], and so on. However, the dielectric loss of BFN is very high, which limits its practical application. Consequently, how to lower the dielectric loss of BFN and simultaneously keep its giant dielectric constant is very necessary. It is well known that $BaTiO_3$ (BT) is a typical perovskite ferroelectric, which possesses high dielectric constant and low dielectric loss.

In this work, BT was incorporated into BFN to lower the dielectric loss of BFN. The phase structure, microstructures and electrical properties of the resultant BFN and BT solid-solution ceramics were also investigated.

2. Experimental

The starting materials of $BaCO_3$, Nb_2O_5 and Fe_2O_3 were weighed, mixed and calcined at 1200 °C in air for 2 h to prepare $Ba(Fe_{0.5}Nb_{0.5})O_3$. Meanwhile, the mixture of $BaCO_3$ and TiO_2 was mixed and calcined at 1200 °C in air for 2 h to synthesize $BaTiO_3$. All the starting materials were from Sinopharm Chemical Reagent, Shanghai, China and their purities are all higher than 99%. The above BFN and BT were ground into

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powder and mixed homogeneously. The mixtures of $(1-x)$Ba$(Fe_{0.5}Nb_{0.5})O_3$–$x$$BaTiO_3$ (abbreviated as $(1-x)$BFN–xBT) with $x = 0$, 0.1, 0.2, 0.3 and 0.4 were pressed into discs after adding 5 wt% PVA. The x value is the mass fraction of $BaTiO_3$. Final sintering was carried out at 1350 °C. The phase structure of the $(1-x)$BFN–xBT ceramics were detected by an X-ray diffractometer (XRD) with Cu Kα radiation (Rigaku D/MAX-2400, Japan). The microstructures of the $(1-x)$BFN–xBT ceramics were analyzed using a scanning electron microscope (SEM) (JEOL JSM-6460, Japan). The electrical properties of the $(1-x)$BFN–xBT ceramics were measured by an impedance analyzer (E4980A, Agilent, Palo Alto, CA).

3. Results and discussion

Fig. 1 shows the XRD patterns of the $(1-x)$BFN–xBT ceramics with different BT concentrations ($x = 0.1$, 0.2, 0.3, 0.4). The index of the diffraction peaks was carried out using a computer package based on least squares refinement method (JADE), as well as the calculation of lattice parameters, which were listed in Table 1. It is found that all the samples are of single-phase with a monoclinic structure, which is consistent

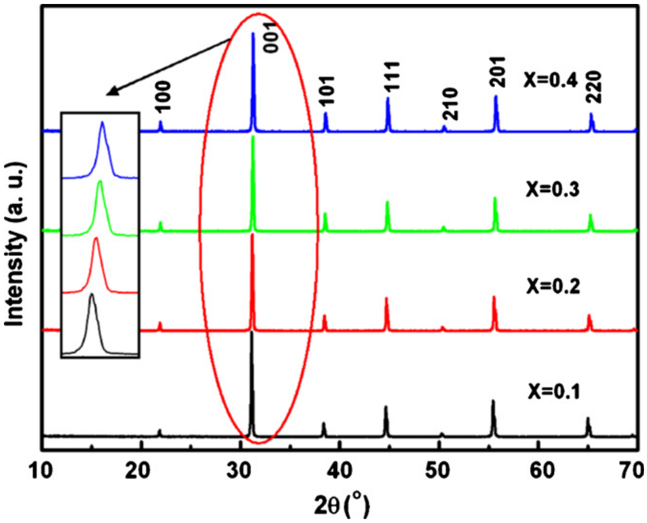

Fig. 1. XRD patterns of the $(1-x)$BFN–xBT ceramics with different BT concentrations ($x = 0.1$, 0.2, 0.3, 0.4), where the inset is the magnification image of peak (0 0 1).

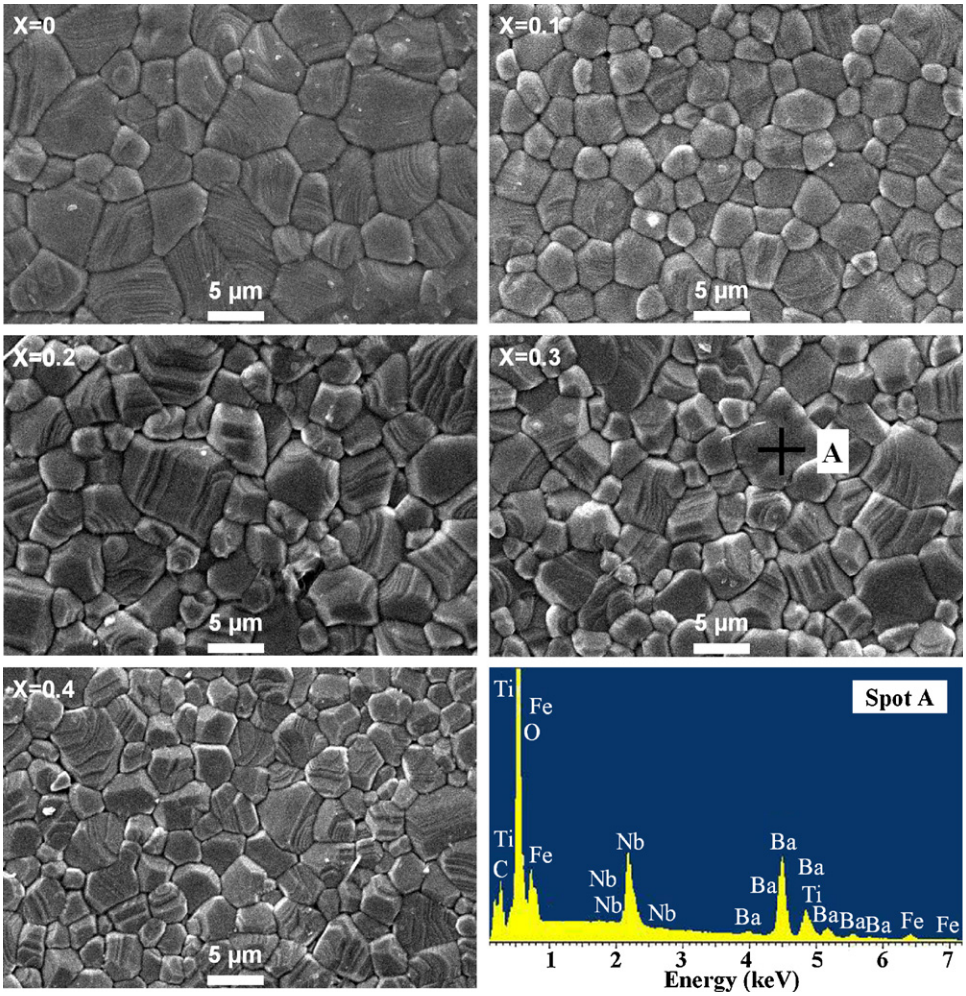

Fig. 2. SEM micrographs of the $(1-x)$BFN–xBT ceramics with different BT concentrations ($x = 0$, 0.1, 0.2, 0.3, 0.4) and EDS analysis results of the 0.7BFN–0.3BT ceramic (lower right).

Table 1
Structural data for the $(1-x)$BFN–xBT ceramics with different BT concentrations ($x = 0$, 0.1, 0.2, 0.3, 0.4).

Sample	Structure	a (Å)	b (Å)	c (Å)	β (°)
$x = 0.1$	Monoclinic	4.0570	4.0546	2.8712	90.13
$x = 0.2$	Monoclinic	4.0503	4.0467	2.8659	90.04
$x = 0.3$	Monoclinic	4.0438	4.0407	2.8610	90.10
$x = 0.4$	Monoclinic	4.0392	4.0369	2.8576	90.13

with the results obtained by Saha and Sinha [14], Ke et al. [16] and Singh et al. [18]. It can also be seen that with increasing x value all the peaks shift to higher angles indicating the decrease of lattice parameters due to the incorporation of smaller Ti^{4+} in B site of the perovskite. The above phenomena also indicate that BT and BFN have completely formed solid solutions. Moreover, compared with $Ba(Fe_{0.5}Nb_{0.5})O_3$–$SrTiO_3$ solid solutions [18], the lattice parameters of the as-prepared BFN–BT ceramics are larger while the β values are smaller due to the fact that the size of Ba^{2+} is larger than that of Sr^{2+} and no A site substitution occurs in the present ABO_3 perovskite solid solutions.

Fig. 2 displays the SEM micrographs of the natural surface of $(1-x)$BFN–xBT ceramics ($x = 0$, 0.1, 0.2, 0.3, 0.4) and EDS analysis results of the 0.7BFN–0.3BT ceramic (lower right). It can be seen that the microstructures of all the samples are very dense and few pores can be observed at the grain boundaries. For the pure BFN ($x = 0$), the grain size is above 5 μm. With increasing x value, the grain size reduces, indicating that the incorporation of BT can fine the microstructure of BFN, which is consistent with the results of the incorporation of $SrTiO_3$ into BFN [18]. Moreover, the spiral growth steps can be observed for all the samples and they become more and more obvious with increasing x value. The phenomenon might be due to the fact that the doping of Ti^{4+} could give rise to some defects, which induces the spiral growth. From the EDS analysis result of the grain of the 0.7BFN–0.3BT ceramic, it can be easily seen that the element composition of the grain is Ba, Fe, Nb, Ti and O, confirming that BT and BFN have completely formed solid solutions.

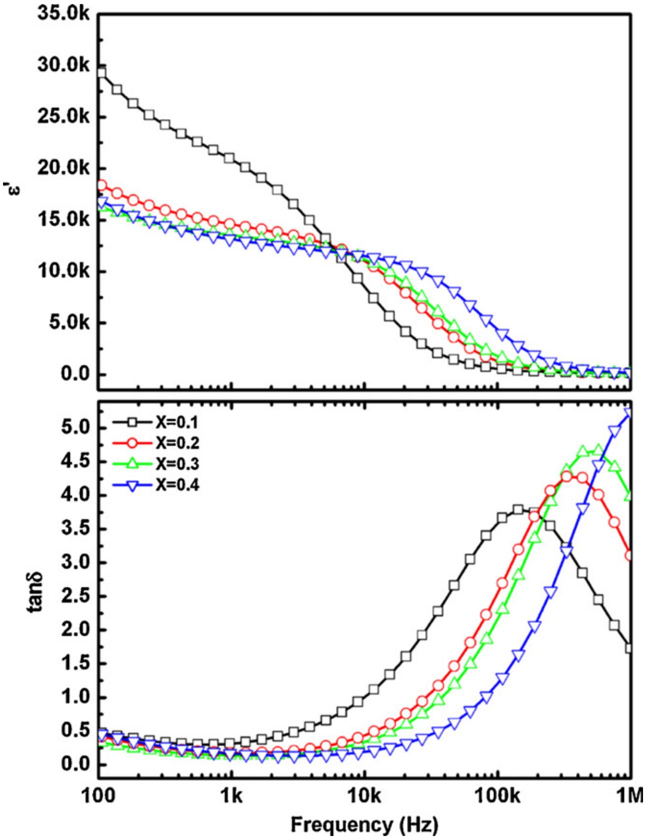

Fig. 3. Logarithmic frequency dependence of the dielectric properties of the $(1-x)$BFN–xBT ceramics with different BT concentrations ($x = 0.1$, 0.2, 0.3, 0.4).

Fig. 3 shows the logarithmic frequency dependence of the dielectric properties of $(1-x)$BFN–xBT ceramics with different BT concentrations ($x = 0.1$, 0.2, 0.3, 0.4). As shown in Fig. 3, for all the samples the dielectric constant (ε') decreases with increasing frequency, which is a normal behavior of dielectrics. Higher values of ε' at lower frequencies are due to the presence of all different types of polarization (i.e., dipolar, atomic, ionic, electronic and Maxwell–Wagner polarizations) in the materials. At higher frequencies, some of the above-mentioned polarizations cannot follow the alternating field and may have less contribution to ε'. When further increasing the frequency to a certain value the ε' shows a step decrease and at the same time the dielectric loss ($\tan\delta$) shows a relaxation peak, which indicates that all the samples have a Debye-like relaxation due to the relaxation nature of BFN [12]. It is worth noting that the $\tan\delta$ of $(1-x)$BFN–xBT ceramic is far lower than that of the pure BFN ceramic. The ε' and $\tan\delta$ at 1 kHz of the pure BFN ceramic is about 39,000 and 1.5, respectively (not shown here). Whereas the $\tan\delta$ of the as-sintered $(1-x)$BFN–xBT ceramics is about 0.14–0.32, indicating that the incorporation of BT could significantly reduce the $\tan\delta$ of BFN ceramic. The ε' at 1 kHz of the as-sintered $(1-x)$BFN–xBT ceramics is about 13,300–21,000, which is still very high, although it is lower than that of pure BFN ceramic. It can also be found that the incorporation of BT can improve the frequency stability of the dielectric properties of BFN.

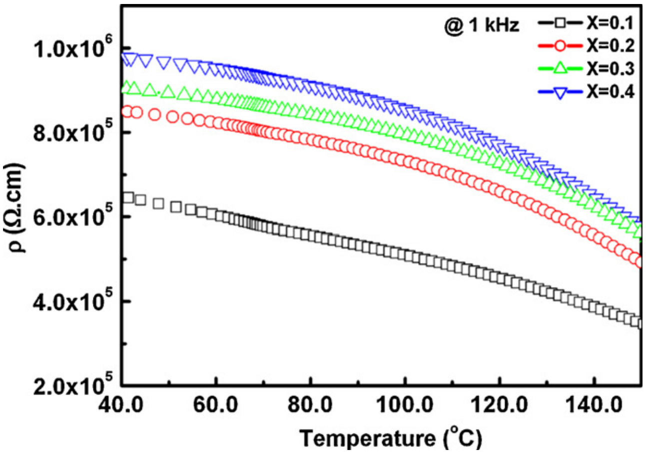

Fig. 4. Temperature dependence of the ac resistivities of the $(1-x)$BFN–xBT ceramics with different BT concentrations ($x = 0.1$, 0.2, 0.3, 0.4).

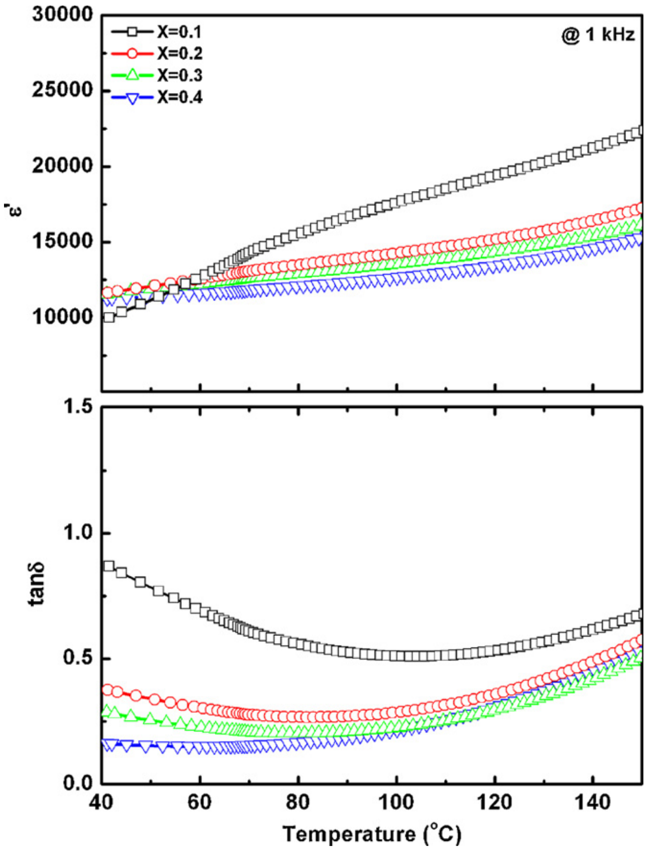

Fig. 5. Temperature dependence of the dielectric properties of the $(1-x)$BFN–xBT ceramics with different BT concentrations ($x = 0.1$, 0.2, 0.3, 0.4).

The temperature dependency of the ac resistivities (ρ) at 1 kHz of the $(1-x)$BFN–xBT ceramics is plotted in Fig. 4. For $x = 0.1$, the ρ is low due to the presence of Fe^{2+}, as suggested by Ananta and Thomas [19]. It can be found that the ρ increases with increasing BT concentrations due to the fact that the doping of high-valence Ti^{4+} could suppress the occurrence of Fe^{2+} and thus increase the ρ of BFN.

Fig. 5 shows the temperature dependence of the dielectric properties of the $(1-x)$BFN–xBT ceramics with different BT concentrations ($x = 0.1$, 0.2, 0.3, 0.4). For $x = 0.1$, the ε' increases obviously with temperature, However, as $x \geq 0.2$, the increasing tendency of the ε' with temperature becomes slight because the doping of high-valence Ti^{4+} could improve the resistivity of BFN, as mentioned above. It can also be seen that the doping of Ti^{4+} can reduce the tan δ of BFN and improve the temperature stability of the dielectric properties of BFN.

4. Conclusions

$(1-x)$BFN–xBT ceramics with giant dielectric constants and low losses were prepared by the conventional solid-state method. The $(1-x)$BFN–xBT ceramics are of monoclinic structure and possess dense microstructures. Also the incorporation of BT can fine the microstructure of BFN. The spiral growth steps can be observed and become more and more obvious with increasing BT concentrations due to the occurrence of defects. The incorporation of BT can significantly reduce the dielectric loss and improve the frequency and temperature stability of the dielectric properties of BFN. The dielectric constants and dielectric losses at 1 kHz of the as-prepared $(1-x)$BFN–xBT ceramics are about 13,300–21,000 and 0.14–0.32, respectively, indicating that they are promising candidate materials for use in capacitors.

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